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Long-time self-diffusion coefficient in colloidal suspensions: theory versus simulation

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Abstract. The long-time self-diffusion coefficient of a colloidal fluid interacting via a Yukawa potential and obeying Brownian dynamics is calculated by computer simulations for different parameters of the Yukawa potential over a broad range of densities. As two extreme cases, the hard sphere and the unscreened Coulomb interaction are also included. The simulation results are compared with different theoretical expressions. In general, it is found that a kinetic-like theory that incorporates both the exact short-time behaviour of the friction kernel and the two-particle dynamics describes the simulational data best. Also, simulations and theories for the self-diffusion in two-dimensional Brownian Yukawa fluids are compared, where the same qualitative behaviour is found.

1. Introduction

In a concentrated suspension of colloidal particles embedded in a solvent, the long-time self-diffusion coefficient of the colloidal particles, D, is significantly smaller than the short-time diffusion constant D_0. Whereas the latter results from random kicks of the solvent and is determined in terms of the solvent friction and the temperature, the long-time self-diffusion is strongly affected by the repulsive interparticle interactions. Furthermore, both quantities depend on hydrodynamic interactions mediated by the solvent. These complicated interactions can be safely ignored if their range, characterized by a hydrodynamic radius, is much smaller than the range of the interparticle interaction. This is the case, for example, in highly charged colloidal suspensions which already show a well-pronounced structure even for very small packing fractions. For suspensions whose interactions are dominated by excluded volume effects only, however, hydrodynamic interactions are very important.

Different experimental techniques like dynamical light scattering [1], forced Rayleigh scattering [2, 3] and fluorescence recovery after photobleaching [4], have been used to measure the long-time self-diffusion coefficient for both charge- and sterically-stabilized colloidal suspensions. Recently it was found that the ratio of short- and long-time self-diffusion coefficients, D/D_0, has a universal value very close to 0.1 on the freezing line of a colloidal fluid which constitutes a dynamical phenomenological freezing rule [5]. In this paper, we shall focus on simulations and theories for the self-diffusion coefficient D.

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In particular, we study how D depends on the nature of the interparticle forces and on the density of the colloidal particles. Henceforth, we shall not consider hydrodynamic interactions explicitly. Then, the short-time diffusion coefficient is given by

$$D_0 = k_B T/6\pi\eta R \equiv k_B T/\xi_0 \tag{1}$$

where η and ξ_0 are the solvent viscosity and friction, respectively, while T is the temperature and R the radius of the colloidal particle. On a 'short' timescale (which is still large compared to that of momentum relaxation of the colloidal particles), the particle motion is simple Brownian with the short-time diffusion constant D_0. The particle interaction is modelled by a pairwise Yukawa potential, being the electrostatic part of the familiar DLVO potential [6,7]

$$V(r) = U_0\sigma \exp[-\lambda(r-\sigma)/\sigma]/r \tag{2}$$

where U_0 sets the energy and σ the length scale. This potential is a good description for the interaction of a dilute charge-stabilized colloidal suspensions whereas it breaks down for a concentrated suspension where many-body interactions also become relevant [8]. The steepness and range of the Yukawa potential depends sensitively on the screening parameter λ. For $\lambda = 0$, the interaction is Coulombic, i.e. the system described is a classical one-component plasma (OCP) usually defined with a homogeneous neutralizing background, whereas for $\lambda \to \infty$ the interaction becomes hard-sphere-like. Consequently, the hard-sphere (HS) and OCP systems are included as special extreme cases, and the Yukawa interaction can also be understood to interpolate smoothly between these two limiting cases of hard and very soft cores.

A systematic study of the long-time diffusion coefficient has only been performed for hard spheres. There have been both Brownian dynamics simulations for different densities [9,10] as well as theoretical investigations [11–14]. In particular, it was shown [13] that an Enskog-like theory describes the data well up to high hard-sphere densities. Although the study of a Brownian hard-sphere system is useful and justified as a model system of statistical mechanics, we emphasize that in a real sterically stabilized colloidal suspension hydrodynamic interactions significantly alter the behaviour. This model therefore cannot be compared directly with experimental data. This is different, however, for the Yukawa potential since there hydrodynamic interaction can be ignored, at least in the weak-screening regime. Our studies of a Yukawa system are thus motivated by two different facts. First, the model is more realistic as regards direct comparison with experiments. Second, more fundamentally, it is interesting to study how the self-diffusion is influenced by the 'softness' of the interparticle interaction. Our work is divided into two parts. First, we present Brownian dynamics computer simulation data for the long-time self diffusion in a Yukawa system. In particular, the dependence on the screening parameter λ is studied. Second, we test different theoretical expressions for the self-diffusion coefficient. To get explicit results from such expressions, one usually needs static input data, such as the pair correlation function $g(r)$ or the structure factor $S(k)$. Here, all the static input data needed to compute theoretical values are also taken from the simulations in order to get a clear-cut estimate for the validity of a theory.

Recently, *two-dimensional* colloidal liquids were prepared by confining charged colloidal particles between charged plates [15]. The Yukawa model (2) remains a simple, though approximate, [16,17] description for the interaction of the two-dimensional interparticle interaction. Whereas in a two-dimensional *atomic* system, the diffusion coefficient is not

well defined [18], it does exist for a two-dimensional Brownian system provided the solvent friction ξ_0 is finite. This is due to the fact that in a Brownian system the long-time tail of the velocity autocorrelation function decays faster than for a corresponding atomic system [19]. In this paper, we also compare simulational data and theories for the long-time self-diffusion for the two-dimensional Yukawa fluid.

The paper is organized as follows. First, we briefly describe the Brownian dynamics simulation method in section 2. Then, we review existing theories in section 3. The theoretical results for the long-time self-diffusion coefficient are compared with the theoretical data in section 4. Finally, we conclude and give an outlook in section 5.

2. Brownian dynamics simulations

The Brownian dynamics (BD) simulations are based on a finite-difference integration of the irreversible Langevin equations of motion [20, 21]. If hydrodynamic interactions are neglected, the (three-dimensional) particle positions $\boldsymbol{r}_i$ at a time $t + \Delta t$ are gained from the old positions at time t as follows:

$$\boldsymbol{r}_i(t + \Delta t) = \boldsymbol{r}_i(t) + \frac{1}{\xi_0}\boldsymbol{F}_i(t)\Delta t + (\Delta \boldsymbol{r})_R + O((\Delta t)^2) \tag{3}$$

where $i = 1, ..., N$ labels the N particles, ξ_0 is the solvent friction and $\boldsymbol{F}_i$ is the total interparticle force on particle i derived from the Yukawa interaction (2). Furthermore, $(\Delta \boldsymbol{r})_R$ is a random displacement due to solvent collisions, which is sampled from a Gaussian distribution of zero mean and variance

$$\overline{(\Delta \boldsymbol{r})_R^2} = 6D_0\Delta t. \tag{4}$$

This means that the motions of the particles for short times is diffusive, with the short-time diffusion constant D_0 related to the solvent friction via (1). The term D_0 defines the natural timescale $\tau_B = \sigma^2/D_0$ and also provides the natural unit to measure the long-time self-diffusion coefficient D that is defined by

$$D = \lim_{t\to\infty} \frac{1}{6t} W(t) \tag{5}$$

with $W(t)$ being the mean-square displacement of one selected particle, usually called a tagged particle:

$$W(t) = \langle (\boldsymbol{r}_1(t) - \boldsymbol{r}_1(0))^2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} (\boldsymbol{r}_i(t) - \boldsymbol{r}_i(0))^2 \right\rangle \tag{6}$$

where $\langle \ldots \rangle$ is a canonical average. In the second equality in (6) we used the fact that in an equilibrium suspension all particles are equivalent. Actually, it is the second expression that is used in a simulation, as this gives much better statistics. Due to the interparticle interaction, D is smaller than D_0, in general. Alternatively, one can define D by the differential expression

$$D = \lim_{t\to\infty} \frac{1}{6} \frac{\mathrm{d}}{\mathrm{d}t} W(t). \tag{7}$$

We use a periodically repeated cubic simulational box of volume V with $N = 500$ particles and generate particle trajectories according to (3) with a sufficiently small timestep Δt. The actual value of Δt depended on the softness of the potential; it was chosen between $0.0003\tau_B$ (for $\lambda = 0$) and $0.000\,01\tau_B$ (for $\lambda \to \infty$). The starting positions were on an FCC lattice and the system was first equilibrated at high temperature and then gently cooled. During the simulation, the centre of mass of the system was fixed in order to avoid spurious drift of the finite system. After a long equilibration period (of at least $3\tau_B$) statistics were gathered (during a period of $\approx 10\tau_B$) and the time-dependent mean-square displacement $W(t)$ was calculated for a long time $t_L \approx 4\tau_B$. Both expressions (5) and (7) were then used to get D, where the long-time limit is replaced by the value of the mean-square displacement at large finite time t_L. It was found that t_L was long enough to be very close to the long-time limit by checking that the two different expressions of the right-hand sides of (5) and (7) were equal at time t_L. Different runs were done for fixed temperature T and varying particle density $n = N/V$.

For the one-component plasma with neutralizing homogeneous background (OCP), we use an Ewald summation in order to take the interaction of all periodically repeated images into account. For the hard-sphere case, the result depends very sensitively on the magnitude of the time-step [10]. Therefore, the time-step has to be chosen to be much smaller for hard repulsions than for softer interactions.

In two spatial dimensions all the equations are unchanged except that there are now two-dimensional position vectors $r_i(t)$, and six in the right-hand sides of (4), (5), (7) has to be replaced by four. The simulations in two dimensions are quite similar. We now use a periodically square box with $N = 529$ particles and start from a simple square lattice. Again, the long-time diffusion coefficient is calculated using both expressions (5) and (7), and for long times agreement is found. For Brownian hard discs, similar simulation studies have recently been performed by Schärtl and Sillescu [22].

3. Theories

Recently a new formalism for the calculation of the self-diffusion coefficient has been derived [13]. It is based on ideas used earlier in kinetic theories of dense fluids [23]. These ideas were applied to analyze the many-body Smoluchowski equation describing the Brownian dynamics of a colloidal suspension. Here we first review the main points of the new approach and state its results. Then we move on to review briefly some older theories for the self-diffusion coefficient.

The main idea of [13] is to express the self-diffusion coefficient D in terms of the friction coefficient ξ_L:

$$D = \frac{k_B T}{\xi_L}. \tag{8}$$

The friction coefficient is the long-wavelength long-time limit of the friction kernel $\xi(r; t)$:

$$\xi_L = \lim_{z\to 0}\lim_{k\to 0}\int_0^\infty dt \int dr e^{-zt+ik\cdot r}\xi(r; t) \tag{9}$$

which is defined through the constitutive relation between the current of the tagged particle and the tagged-particle density gradient:

$$\int_0^\infty dt' \int dr'\xi(r - r'; t - t')j(r'; t') = -k_B T\frac{\partial}{\partial r}n_s(r; t). \tag{10}$$

Here n_s is the tagged-particle density and j is the current of the tagged particle. The current is defined through the continuity equation

$$\frac{\partial}{\partial t} n_s(r; t) = -\frac{\partial}{\partial r} j(r; t). \tag{11}$$

Note that the right-hand side of (10) is the osmotic (or entropic) force.

Finally, to calculate the friction kernel one uses the following expression for the current, which can be derived from the first equation of the BBGKY-like hierarchy for the many-particle Smoluchowski equation [13, 24]:

$$j(r_1; t) = -D_0 \frac{\partial}{\partial r_1} n_s(r_1; t) + \frac{1}{\xi_0} \int \mathrm{d}r_2 F_{12} \delta n_2(r_1, r_2; t). \tag{12}$$

Here F_{12} is the force on the particle at r_1 exerted by the particle at r_2, and δn_2 is the difference between the non-equilibrium pair distribution function and the local equilibrium pair distribution function (see [13] for details). The time evolution of δn_2 is described by the following evolution equation, which can be derived from the second equation of the BBGKY-like hierarchy:

$$\begin{aligned}\frac{\partial}{\partial t} \delta n_2(r_1, r_2; t) = &-n \left(\frac{\partial}{\partial r_1} g_2^{\mathrm{eq}}(r_{12}) \right) j(r_1; t) \\ &+ \left[D_0 \frac{\partial^2}{\partial r_1^2} + D_0 \frac{\partial^2}{\partial r_2^2} + \frac{1}{\xi_0} \left(\frac{\partial}{\partial r_1} - \frac{\partial}{\partial r_2} \right) F_{12} \right] \delta n_2(r_1, r_2; t) \\ &+ \frac{n}{\xi_0} \frac{\partial}{\partial r_1} \left(g_2^{\mathrm{eq}}(r_{12}) \int \mathrm{d}r_3 F_{13} \delta n_2(r_1, r_3; t) \right) \\ &- \sum_{i=1}^{2} \frac{1}{\xi_0} \frac{\partial}{\partial r_i} \int \mathrm{d}r_3 F_{i3} \delta n_3(r_1, r_2, r_3; t).\end{aligned} \tag{13}$$

Here g_2^{eq} is the equilibrium two-particle correlation function and δn_3 describes the dynamical three-particle correlations.

To calculate the friction kernel, one now has to solve equation (13) with respect to the non-equilibrium distribution δn_2, substitute the result into (12), rearrange terms containing the current, and compare with the definition of the friction kernel (9). Note that up to this point no approximations have been made. However, (13) is not closed, as it contains the three-particle correlations.

The approach adopted in [13] was first, to keep only the two-particle dynamics, and second, to take into account the enhanced probability of binary encounters. With this aim in view, the three-particle dynamical correlations δn_3 were neglected completely, the third term at the right-hand side was omitted, and the potential of the effective mean force $V^{\mathrm{eff}}(r_{12}) = -k_{\mathrm{B}} T \log g_2^{\mathrm{eq}}(r_{12})$ in the source term in (13) was replaced by its low-density limit. The friction coefficient obtained in this way was essentially the solvent friction plus the low-density correction renormalized by the pair correlation function:

$$\xi_{\mathrm{L}} = \xi_0 - \frac{n}{k_{\mathrm{B}} T V} \int \mathrm{d}r_1 \int \mathrm{d}r_2 \, (\hat{k} \cdot F_{12}) \frac{1}{\Omega_2} (\hat{k} \cdot F_{12}) g_2^{\mathrm{eq}}(r_{12}) \tag{14}$$

where $\hat{k}$ is an arbitrary unit vector and Ω_2 denotes the two-particle Smoluchowski operator:

$$\Omega_2 = D_0 \frac{\partial^2}{\partial r_1^2} + D_0 \frac{\partial^2}{\partial r_2^2} + \frac{1}{\xi_0} \left(\frac{\partial}{\partial r_1} - \frac{\partial}{\partial r_2} \right) F_{12}. \tag{15}$$

The approximations that lead to (14) are essentially the same as those underlying the Enskog kinetic theory of a hard-sphere fluid [23] and its generalizations to continuous potentials [25]. Therefore the theory of [13] is referred to as the Enskog theory for the self-diffusion coefficient of colloidal suspensions.

It was shown in [13] that for a hard-sphere suspension the Enskog theory includes in an exact way short-time contributions to the friction kernel. For a general continuous potential this is no longer true. For soft potentials the Enskog theory greatly overestimates short-time contributions. Therefore we propose a minimal modification of the Enskog theory that includes the exact short-time behaviour of the friction kernel for continuous potentials. To this end, we again keep the two-particle dynamics (we neglect the three-particle term of (13) and omit the third term in the right-hand side), but we also keep the full potential of the effective mean force in the source term in (13). In this way, we obtain the following expression for the friction coefficient:

$$\xi_L = \xi_0 - \frac{n}{V}\int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2\, (\hat{\boldsymbol{k}}\cdot \boldsymbol{F}_{12})\frac{1}{\Omega_2}\left(\hat{\boldsymbol{k}}\cdot\frac{\partial}{\partial \boldsymbol{r}_{12}} g_2^{eq}(r_{12})\right). \tag{16}$$

The modification of the Enskog theory seems to be inconsistent, since we effectively include some three-particle processes. However, we found no other way to include the proper short-time behaviour of the friction kernel and to keep the two-particle Smoluchowski dynamics Ω_2. Moreover, it will be shown in section 4 that results obtained from (16) are in excellent agreement with the simulation results for soft potentials. Note that the modified Enskog expression (16) was also proposed in [24].

There are two other theories available for the calculation of the self-diffusion coefficient. Historically the first one was the mode-coupling theory, which was developed by Mori and Zwanzig [26] and applied to colloids by Hess and Klein [19]. Its starting point is the exact expression for the tagged-particle intermediate scattering function. This expression is then analyzed and approximated using the ideas borrowed from the mode-coupling theories of simple liquids. The final result is a non-linear self-consistent equation for the scattering function. This equation also involves the so-called collective scattering function, for which another self-consistent equation is written down. Since non-linear self-consistent equations are difficult to solve one usually approximates them further, introducing short-time limits of the scattering functions into friction kernels (for details see [19] and references cited therein). In this way one obtains the following expression for the friction coefficient:

$$\xi_L = \xi_0\left(1 + \frac{1}{6\pi^2}\int_0^\infty dk k^2 \frac{[S(k)-1]^2}{1+S(k)}\right). \tag{17}$$

Here $S(k)$ is the static structure factor

$$S(k) = 1 + n\int d\boldsymbol{r} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}(g_2^{eq}(r) - 1).$$

Another theory has been proposed by Medina-Noyola [27]. It is based on an analysis of the generalized Langevin equation describing the coupled motion of the tagged particle and the surrounding colloidal suspension. The final result for the friction coefficient is

$$\xi_L = \xi_0\left(1 + \frac{n}{6}\int d\boldsymbol{r}[g_2^{eq}(r) - 1]^2\right). \tag{18}$$

It turns out that numerically the expressions (17) and (18) are very close (see, for example, [14] figure 1). Therefore, in the next section, we compare the Brownian dynamics simulation results with the theoretical predictions based on (14), (16) and (18). With the same basic ideas, all theories can also be constructed in *two* spatial dimensions, where the resulting expressions are quite similar.

An intriguing question concerns an analogy between the dynamics of colloidal and atomic fluids. Recently, de Schepper and co-workers [28] proposed such a mapping between these two different kinds of dynamics by which they got a simple and reasonably accurate expression for D. There are, however, both similarities and differences in the long-time correlation for Newtonian and Brownian dynamics [5, 21]. Therefore, in this paper, we prefer to start directly from Smoluchowski rather than from Liouville dynamics.

Table 1. Simulation data for the ratio D/D_0 for d-dimensional Yukawa systems characterized by a screening parameter λ, temperature k_BT/U_0 and number density $n\sigma^d$. The OCP ($\lambda = 0$) is characterized by the plasma coupling parameter Γ; $\lambda = \infty$ for hard discs. The number in brackets gives the error in D/D_0 of the last digit. For comparison, the amplitude g_m of the first maximum of the equilibrium pair correlation function g_2^{eq} is also shown.

d	λ	k_BT/U_0	$n\sigma^d$	g_m	D/D_0
3	8	1	0.2	1.13	0.88(4)
3	8	1	0.3	1.21	0.77(2)
3	8	1	0.4	1.31	0.68(2)
3	8	1	0.6	1.53	0.55(1)
3	8	1	0.8	1.76	0.41(1)
3	8	1	1.0	2.00	0.332(9)
3	8	1	1.2	2.23	0.223(8)
3	8	1	1.4	2.46	0.145(8)
3	3	0.8	0.2	1.05	0.81(2)
3	3	0.8	0.6	1.20	0.63(1)
3	3	0.8	1.0	1.29	0.56(1)
3	3	0.8	1.6	1.39	0.49(1)
3	3	0.8	3.0	1.51	0.39(1)
3	3	0.8	9.0	1.69	0.301(8)
3	0	—	$\Gamma = 1$	1.00	0.92(2)
3	0	—	$\Gamma = 10$	1.14	0.64(2)
3	0	—	$\Gamma = 20$	1.31	0.53(1)
3	0	—	$\Gamma = 60$	1.74	0.32(1)
3	0	—	$\Gamma = 120$	2.17	0.177(8)
2	∞	—	0.255	1.35	0.67(3)
2	∞	—	0.462	2.06	0.47(3)
2	∞	—	0.694	3.65	0.27(2)
2	8	1	0.2	1.14	0.77(4)
2	8	1	0.4	1.36	0.56(2)
2	8	1	0.6	1.70	0.400(9)
2	8	1	1.	2.70	0.165(9)
2	3	0.8	0.1	1.01	0.83(3)
2	3	0.8	0.2	1.05	0.72(3)
2	3	0.8	0.5	1.26	0.52(1)
2	3	0.8	1.0	1.56	0.370(8)
2	3	0.8	2.0	1.96	0.264(6)

4. Results

Results of the BD simulations and the different theoretical expressions for the long-time self-diffusion coefficient D are summarized in table 1 and are also graphically displayed in figures 1–7. We fixed the potential parameters and the temperature, and varied the particle number density, which is conveniently measured in units of σ^{-3}, σ being the length scale of the Yukawa potential (2). The temperature, on the other hand, is measured by the dimensionless number k_BT/U_0 where U_0 is the energy scale in (2). To calculate explicitly the theoretical expressions, we used the pair distribution function obtained from the simulation. In this way we do not introduce additional approximations, thus only testing the dynamical theory.

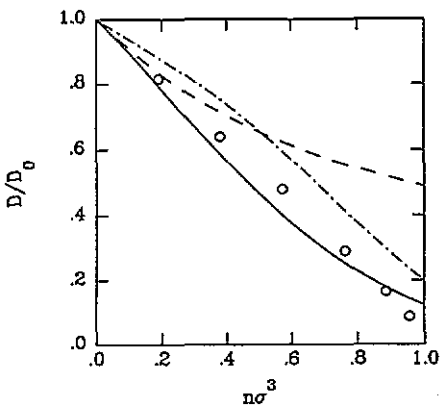

Figure 1. Self-diffusion coefficient divided by its low-density limit D/D_0 as a function of the reduced density $n\sigma^3$ for a three-dimensional hard-sphere suspension, σ denoting the hard-sphere diameter. Circles: Brownian dynamics data of [10]; full curve: Enskog theory (14); broken curve: modified Enskog theory (16); chain curve: theory of Medina-Noyola (18).

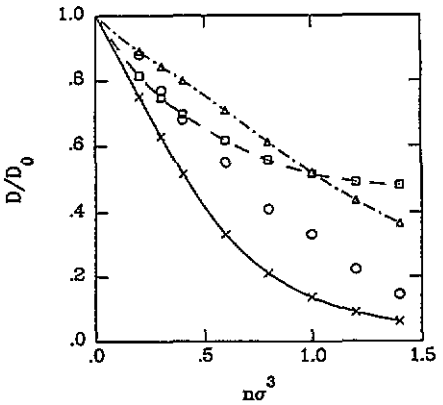

Figure 2. Self-diffusion coefficient divided by its low-density limit D/D_0 as a function of the reduced density $n\sigma^3$ for a three-dimensional Yukawa suspension. Parameters of the Yukawa potential: $\lambda = 8$, $k_BT/U_0 = 1$. Circles: Brownian dynamics results; crosses: Enskog theory (14); squares: modified Enskog theory (16); triangles: theory of Medina-Noyola (18). Curves serve only as guides to the eyes, the actual calculations were performed at the data points.

First, in figure 1, we recapitulate well known results for hard spheres. The predictions of the Enskog theory seem to describe the simulation results best. Note that the theory due to Medina-Noyola, which is also quite reasonable, has a wrong low-density behaviour. The modified Enskog theory gives for the hard-sphere potential a trivial low-density expression for the friction coefficient, $\xi_L = \xi_0(1+\pi n\sigma^3/3)$ and, correspondingly, the results for the self-diffusion are also not accurate. As a comment we remark that, for hard-sphere suspensions, the corrections to the Enskog theory have been calculated [14], which significantly improve agreement with the simulation for the densities up to $n\sigma^3 \approx 0.8$.

In figure 2, we compare the simulations and the theoretical predictions for a continuous but quite steep potential, $\lambda = 8$, $k_BT/U_0 = 1$. Here none of the theories seems to describe the simulation results correctly. Note that for not too high densities the modified Enskog theory is quite close to the simulation data.

Figure 3 contains the simulation data and theoretical predictions for a rather soft potential, $\lambda = 3$, $k_BT/U_0 = 0.8$. Here it is found that the modified Enskog theory agrees

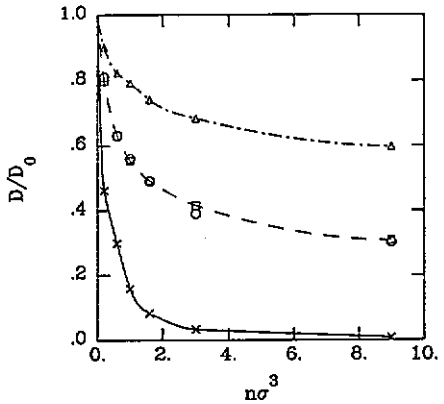

Figure 3. Same as figure 2; but now for a softer Yukawa potential with parameters $\lambda = 3$, $k_BT/U_0 = 0.8$.

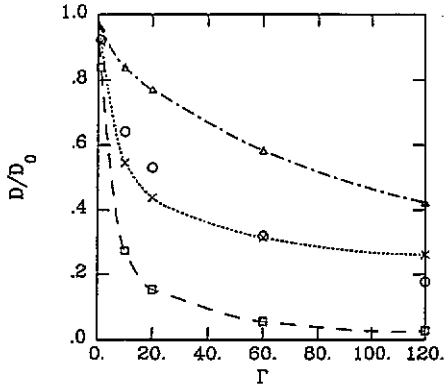

Figure 4. Self-diffusion coefficient divided by its low-density limit D/D_0 as a function of the plasma parameter Γ for a three-dimensional Brownian one-component-plasma. Circles: Brownian dynamics results; squares: modified Enskog theory (16); triangles: theory of Medina-Noyola (18); crosses: modified Enskog theory with a screening length equal to the ionic-sphere radius.

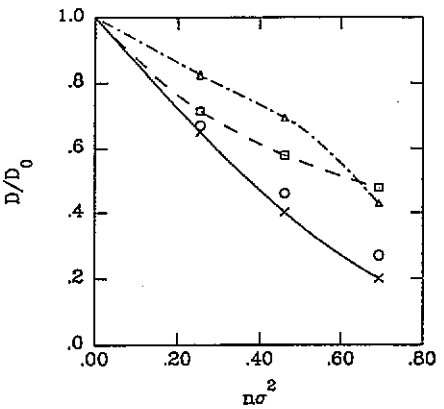

Figure 5. Same as figure 1, but now for Brownian hard discs, σ denoting the hard-disc diameter.

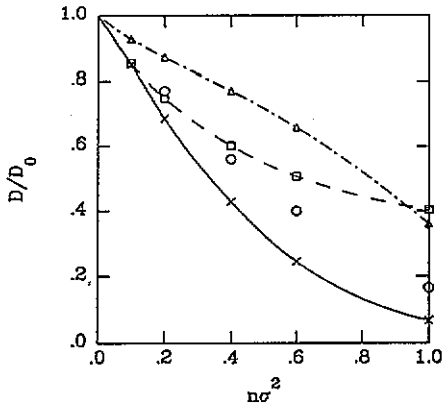

Figure 6. Same as figure 2, but now for a two-dimensional Yukawa suspension with parameters $\lambda = 8$, $k_BT/U_0 = 1$.

surprisingly well with the simulation results. The Enskog theory greatly underestimates the diffusion coefficient whereas the theory of Medina-Noyola give results 50–100% too high. The failure of the Enskog theory might have been expected. It does not incorporate the correct short-time behaviour of the friction kernel. Actually for this very soft potential it greatly overestimates the short-time contributions to the friction coefficient. This will be even more visible for the OCP, where the friction coefficient predicted by the Enskog theory diverges.

In figure 4, we compare the simulations and the theoretical predictions for the OCP. Here, instead of the density, we use the dimensionless plasma coupling constant $\Gamma = U_0\sigma/ak_BT$,

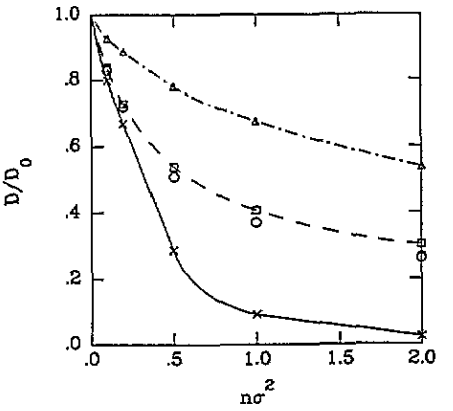

Figure 7. Same as figure 3, but now for a two-dimensional Yukawa suspension with parameters $\lambda = 3$, $k_BT/U_0 = 0.8$.

where a denotes the ion-sphere radius $a = (4\pi/3n)^{1/3}$ [29]. The long-range character of the Coulomb potential causes some additional problems. The Enskog expression for the friction coefficient is divergent due to the slow decay of the potential, whereas the expression of the modified theory is finite. However, it overestimates the friction and correspondingly underestimates the self-diffusion coefficient. The theory of Medina-Noyola, on the other hand, overestimates the self-diffusion coefficient. Note that the Coulomb potential in the two-particle Smoluchowski operator is not screened, whereas one expects that some screening should take place in a plasma. If we introduce somewhat arbitrarily a screening length equal to the ionic-sphere radius into the modified Enskog expression, the results agree quite well with the simulation data. This is shown in figure 4.

Finally, in figures 5–7, we compare the simulations and the theoretical predictions for the two-dimensional suspensions. In particular, we choose a hard disc, a steep and a soft Yukawa potential. We basically find the same scenario as in the three-dimensional case. For hard discs (figure 5), the Enskog theory is now clearly superior to Medina-Noyola's expression (compared to the case of hard spheres). Again, for the soft Yukawa potential, the modified Enskog theory describes the simulation data reasonably well.

5. Conclusions

We have presented simulation data for the long-time self-diffusion coefficient of a Brownian Yukawa system in three and two dimensions. It was found that the self-diffusion coefficient changes much less with increasing density for softer interactions. However it scales roughly with the first maximum g_m of the pair distribution g_2^{eq} which is also displayed in table 1.

The simulation data have been compared with different theories that need static data as an input. In general, dynamical quantities depend much more sensitively on the nature of the interparticle forces than the structural properties. Thus it is generally more difficult to predict the self-diffusion coefficient accurately by a theory that is based on a static input. It was found that for a hard-sphere interaction the Enskog theory is the most accurate. For a strongly screened Coulomb potential essentially no theory describes the simulation data. The modified Enskog theory works very well for moderately screened Coulomb potentials. In conclusion, we think that the important requirement for the dynamical theory is to describe

the short-time behaviour of the friction kernel correctly. The actual time evolution of the kernel can be approximated by that given by the two-particle dynamics. An important exception seems to be the Brownian OCP where one has to introduce a screening of the bare Coulomb interaction. The qualitative features of the different theories do not change in the case of two spatial dimensions.

It would be instructive to compare these results with recent measurements on well characterized dilute charged suspensions [3]. For the experimental system, hydrodynamic interactions can be safely ignored, and the interaction may be modelled by a Yukawa potential according to the DLVO or Poisson–Boltzmann cell model [7]. The thermodynamic parameters and the parameters characterizing the Yukawa potential that are accessible in the experiment of [3] are in the region of relatively weak screening where the modified Enskog theory works well. A systematic comparison of the experimental data with theory and simulation is in progress [30]. For quantitative comparison, effects of polydispersity in the effective charge [31] may also become relevant and should be discussed, too. We further remark that the case of a (quasi)-two-dimensional Brownian liquid, confined between parallel plates, is particularly interesting since real space image methods can be used to probe directly the diffusive dynamics of the colloidal particles [22]. We believe that a careful comparison between experiments and simulations for long-time self-diffusion may lead to definitive information on the interparticle forces determining, for instance, the effective charge used in the Yukawa model.

Another remark concerns the role of hydrodynamic interactions. Although a complete theoretical treatment for self-diffusion is still missing, one may simply map the full dynamics of the system onto that of a reference system without hydrodynamic interactions by using a scaling of the diffusion coefficient proposed by Medina-Noyola [27]. In this sense, all our results should also have relevance in the high screening region, where hydrodynamic interactions become important for concentrated suspensions.

As a final interesting question we note that one may try to establish a connection between the static Hansen–Verlet freezing rule [32] and the dynamical freezing criterion ($D/D_0 = 0.1$) which was put forward in [5]. A possible theoretical connection could be based on the dynamical theories we discussed here, which relate D/D_0 to the pair structure.

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